



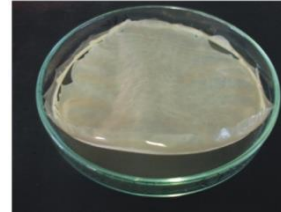
University of Palermo
Department of Physics and Chemistry

CHIMICA DEI MATERIALI

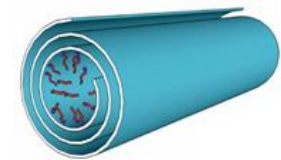
Giuseppe Lazzara, Stefana Milioto

Our recent research activities

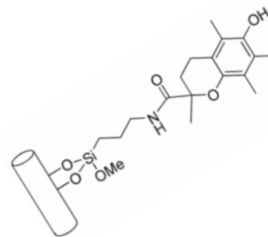
- Bio-nanocomposites based on halloysite



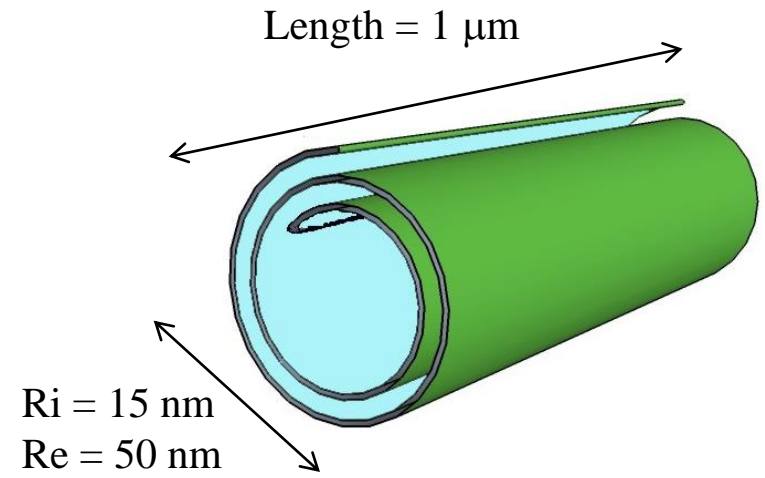
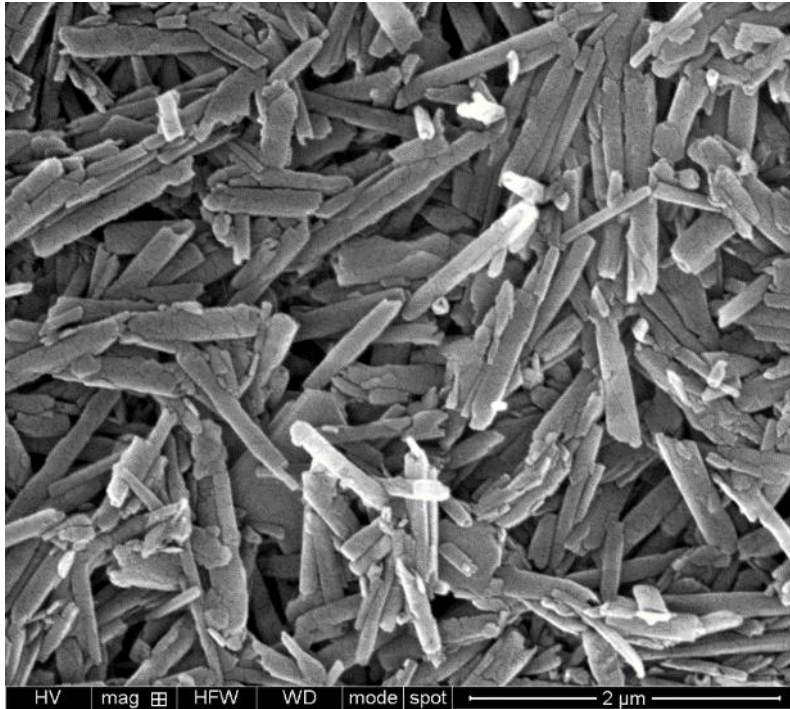
- Halloysite-surfactant hybrid materials



- Chemical modification of Halloysite



Halloysite nanotubes

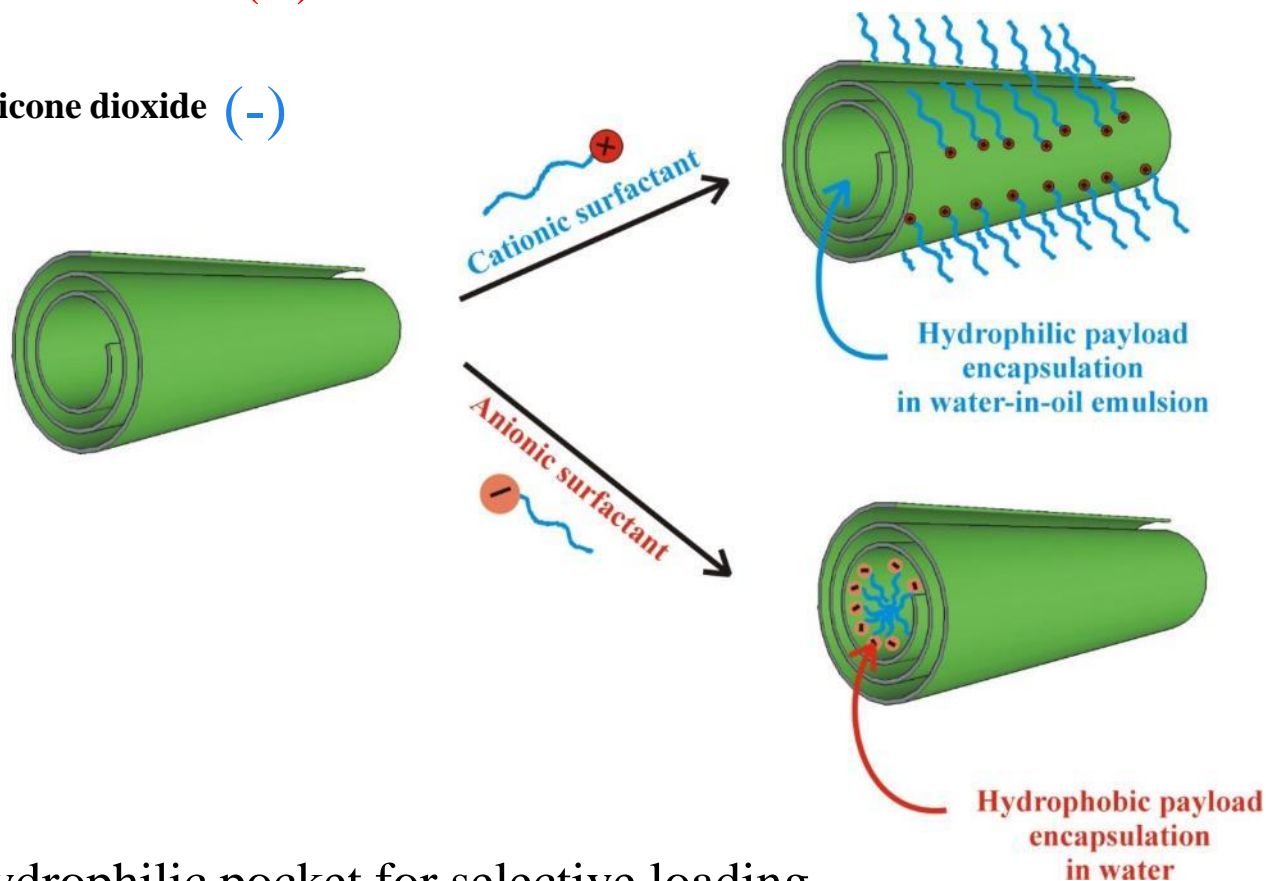


- **Different surface chemistry**
- **Available cavity**

Selective adsorption of surfactants

Inner surface: aluminum oxide (+)

Outer surface: silicone dioxide (-)



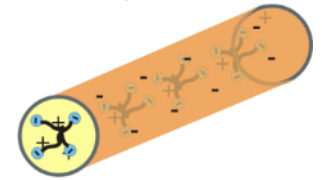
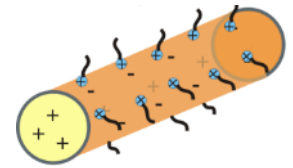
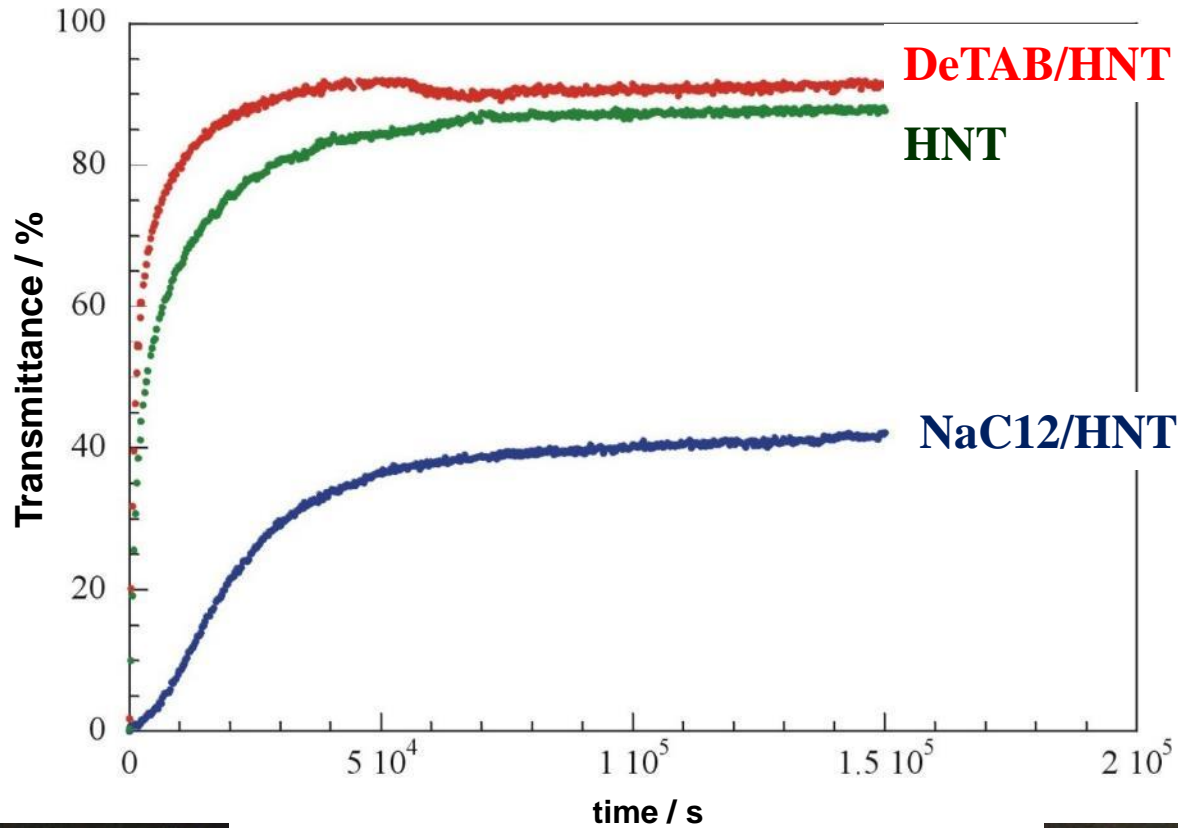
Hydrophobic/hydrophilic pocket for selective loading

Cavallaro, G.; Lazzara, G.; Milioto, S. *J. Phys. Chem. C* **2012**, *116*, 21932

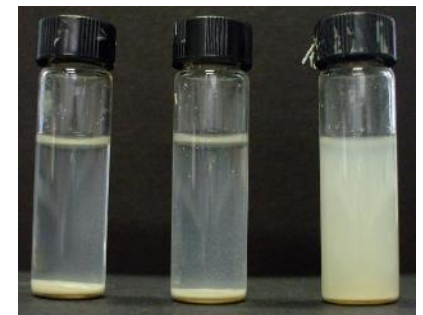
Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F.; Sanzillo, V. *ACS Appl. Mater. Interfaces* **2014**, *6*, 606

Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F. *Langmuir* **2015**, *31*, 7472–7478

Colloidal stability



after 40 hours

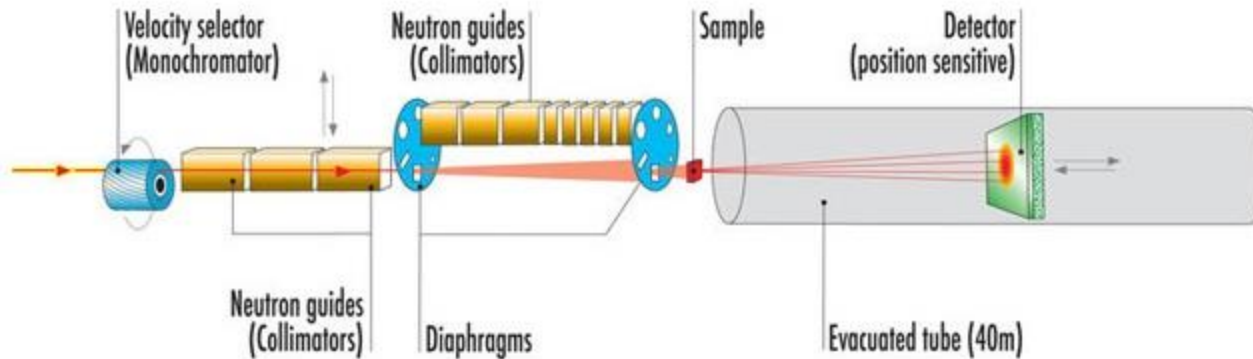


DeTAB/HNT **HNT** **NaC12/HNT**

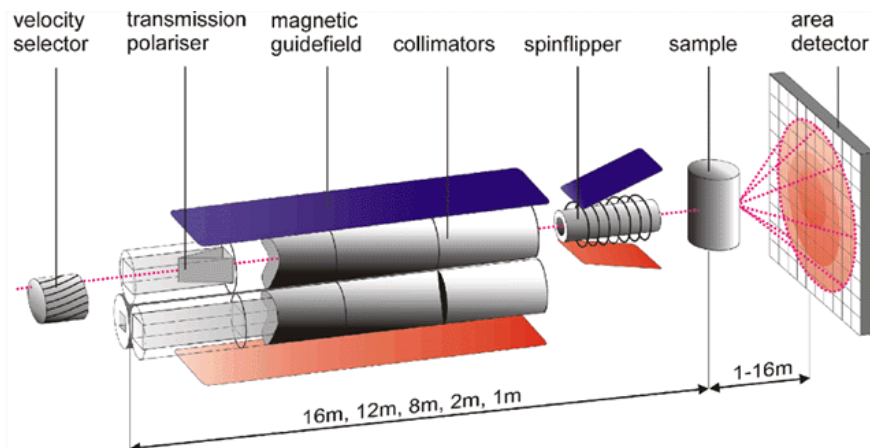
DeTAB/HNT **HNT** **NaC12/HNT**

The structure of the hybrid material

Small Angle Neutron Scattering



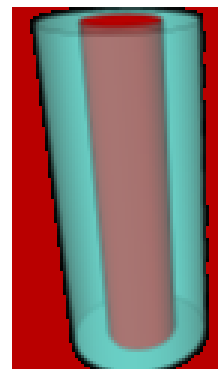
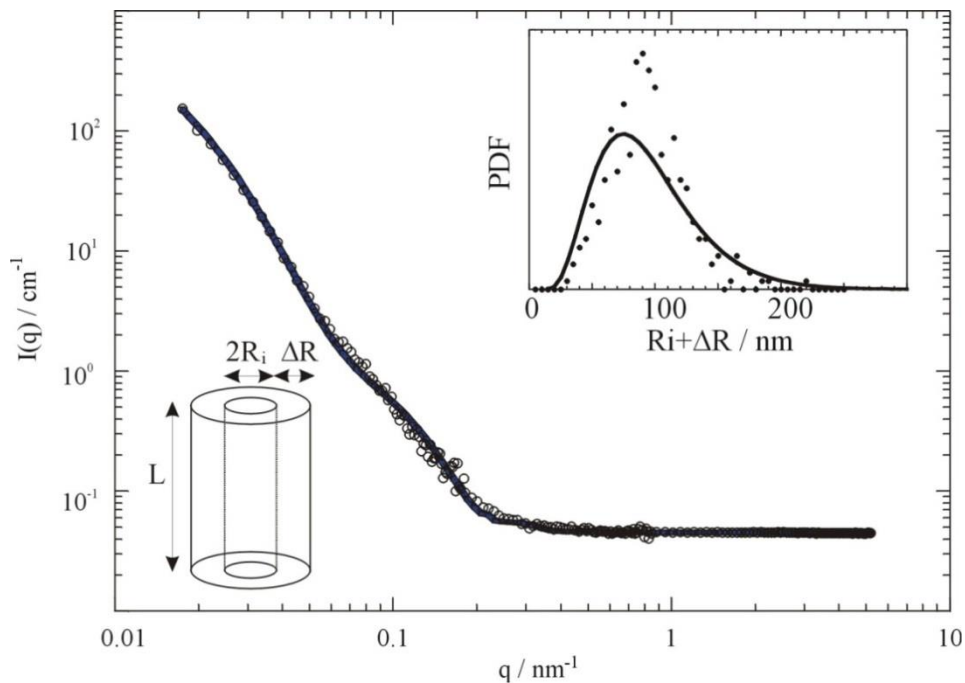
ILL Neutron facility in Grenoble (France)



BENSCH facility in Berlin (Germany)

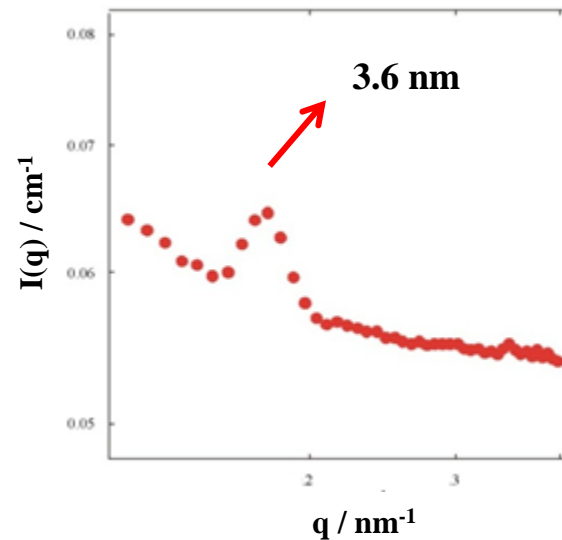
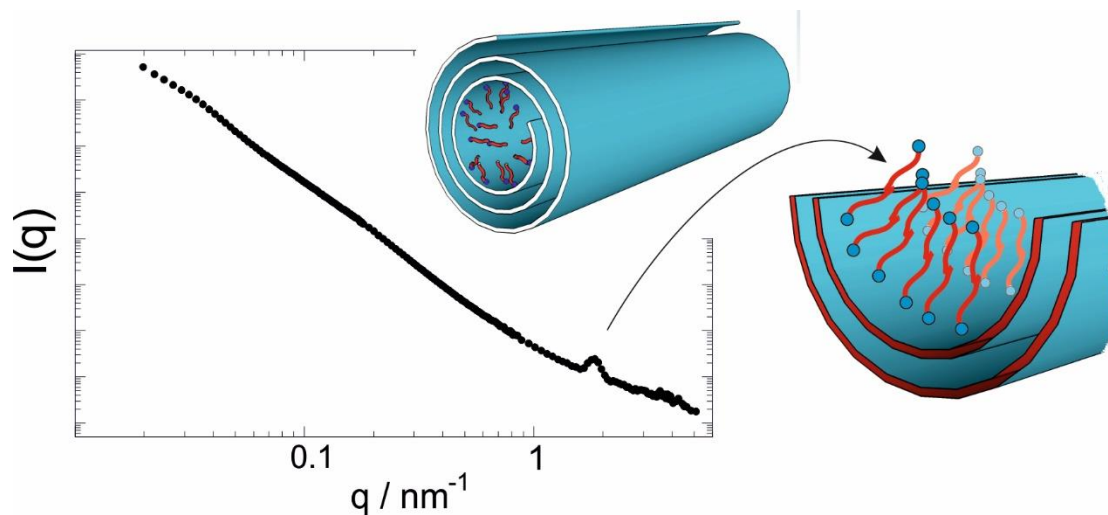
Small Angle Neutron Scattering (SANS)

HNT/D₂O

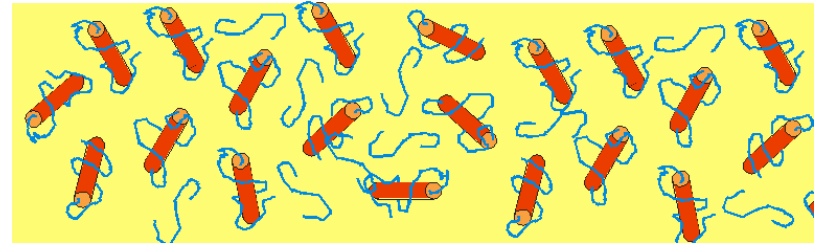
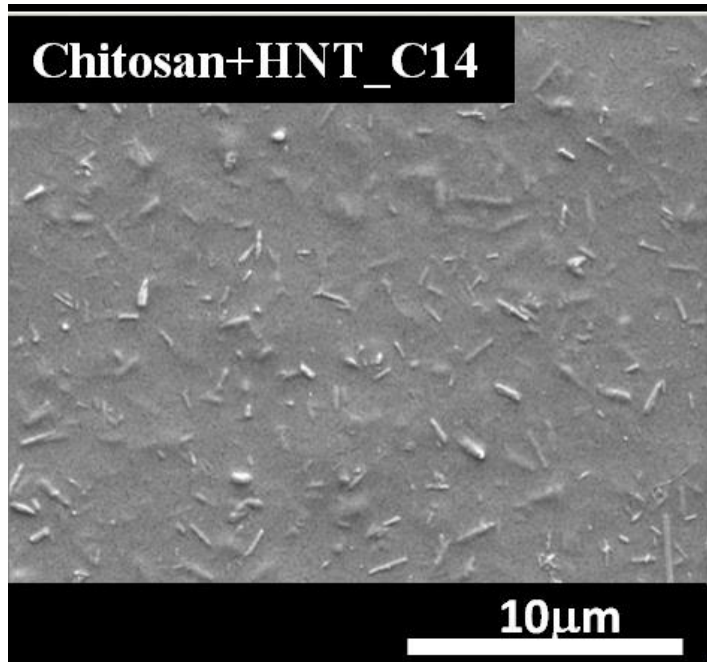


Hollow cylinder

$R_i = 15 \text{ nm}$
 $R_e = 70 \text{ nm}$
Length = 500 nm

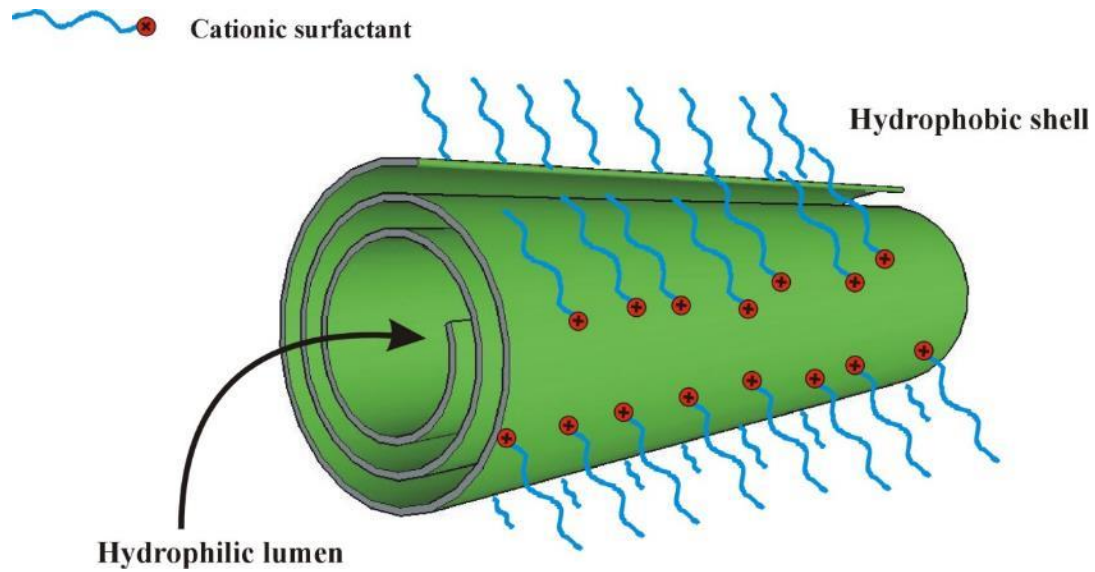


Eco-friendly sponge for organic solvents

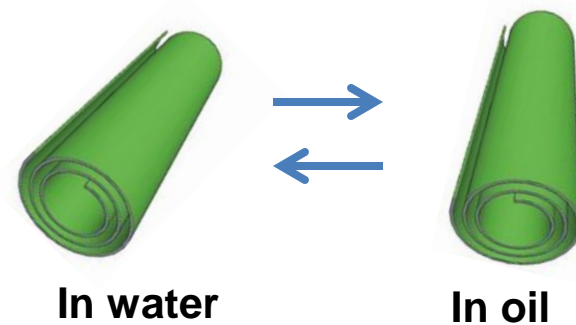
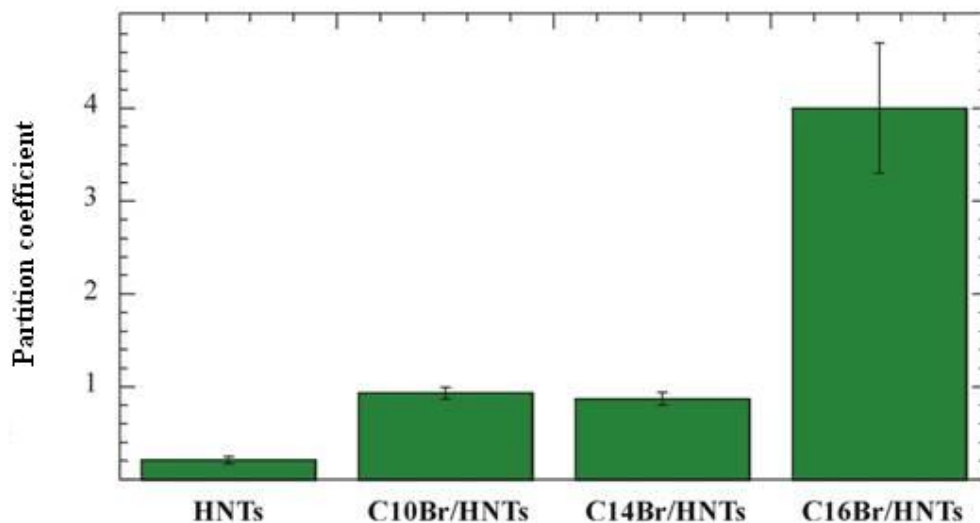
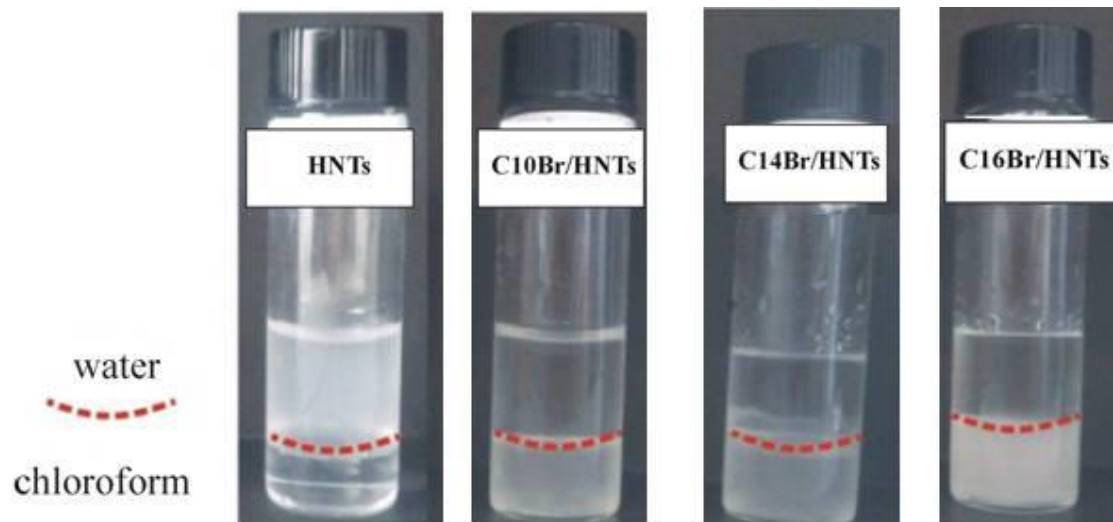


Good nanoclay dispersion in the polymer matrix

Reverse inorganic micelles



Partition between water and oil



Applications for Cultural Heritage

Cleaning



Consolidation:

Paper

Cavallaro, G; Lazzara, G; Milioto, S; Parisi, F.
Halloysite nanotubes with fluorinated cavity: an innovative consolidant
for paper treatment
Journal of Clay Minerals **2016**, *just accepted*

Wood

Cavallaro G, Lazzara G, Milioto S, Parisi F, Sparacino V.
Thermal and dynamic mechanical properties of beeswax-halloysite nanocomposites
for consolidating waterlogged archaeological woods.
Polymer Degradation and Stability. 2015;120:220–5.

Waterlogged Archaeological Woods



17th century ship – Vasa Museum, Stockholm

General conservation state:

- highly degraded
- high porosity (even more than 90% !)
- low mechanical resistance



drying

Consolidation is a key issue!

Macroscopic observation of beeswax/HNT nanocomposites

Beeswax



Beeswax + HNT 60 %



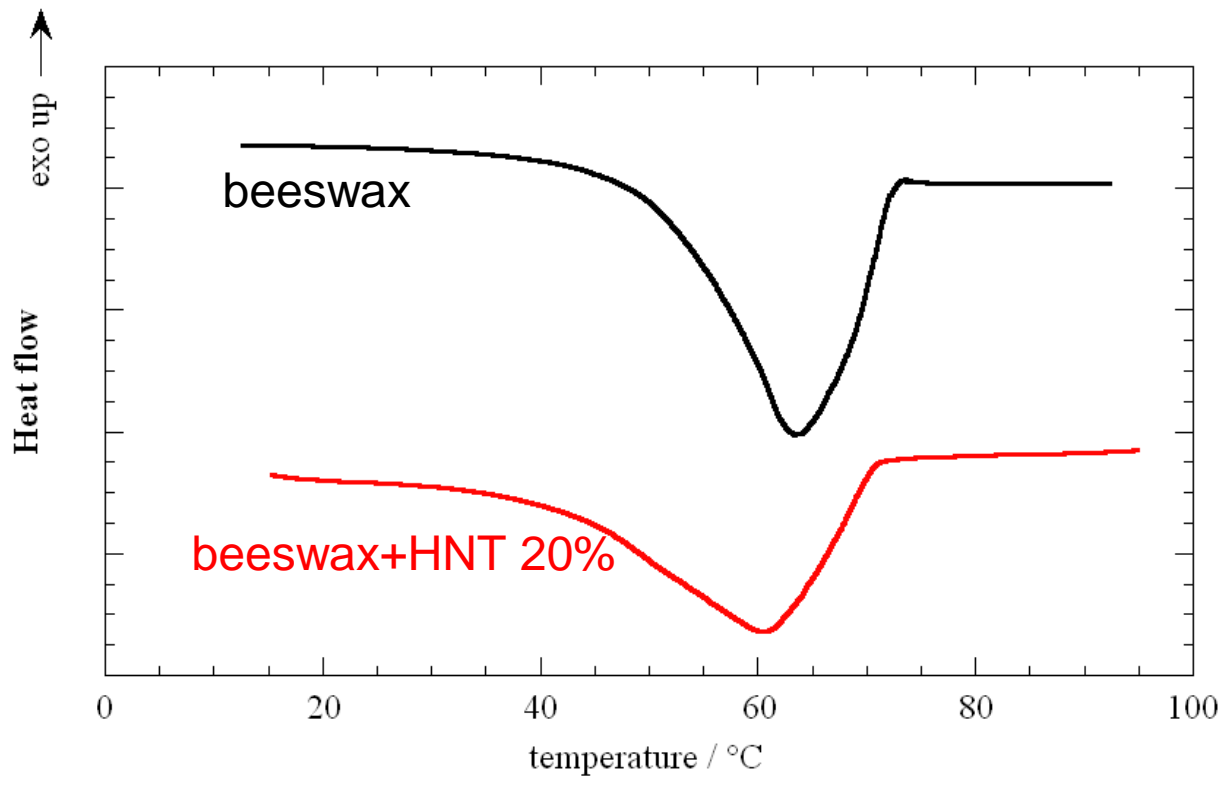
T : 75 °C
t : 0 s

T : 75 °C
t : 7 min

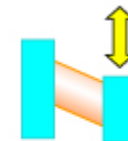
Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F.; Sparacino, V. *Polym.Degrad. Stab.* 2015, 120, 220–225.

Zhao, Y.; Thapa, S.; Weiss, L.; Lvov, Y. *Advanced Engineering Materials* 2014, 16, 1391–1399.

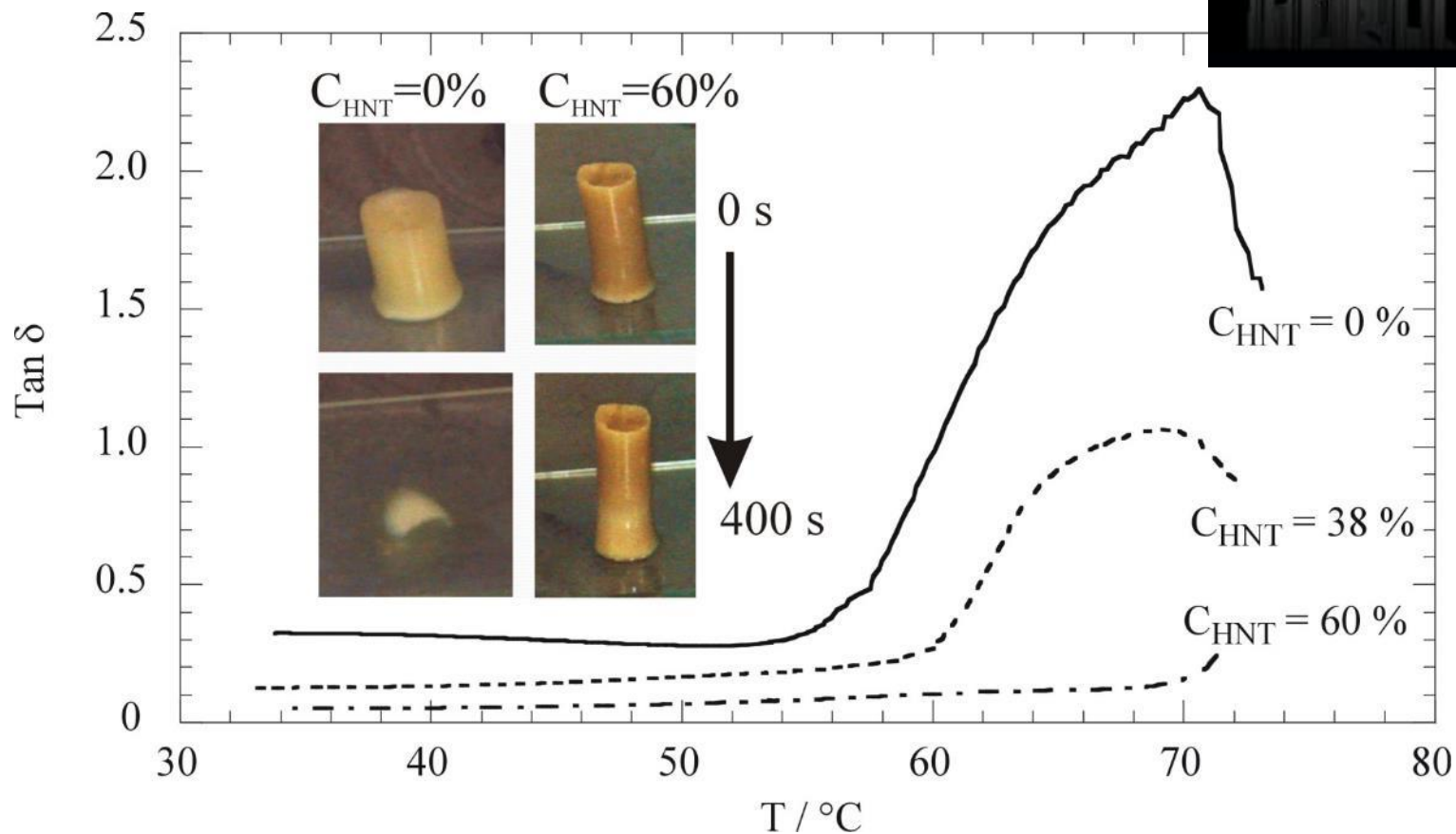
DSC characterization of beeswax/HNT nanocomposites



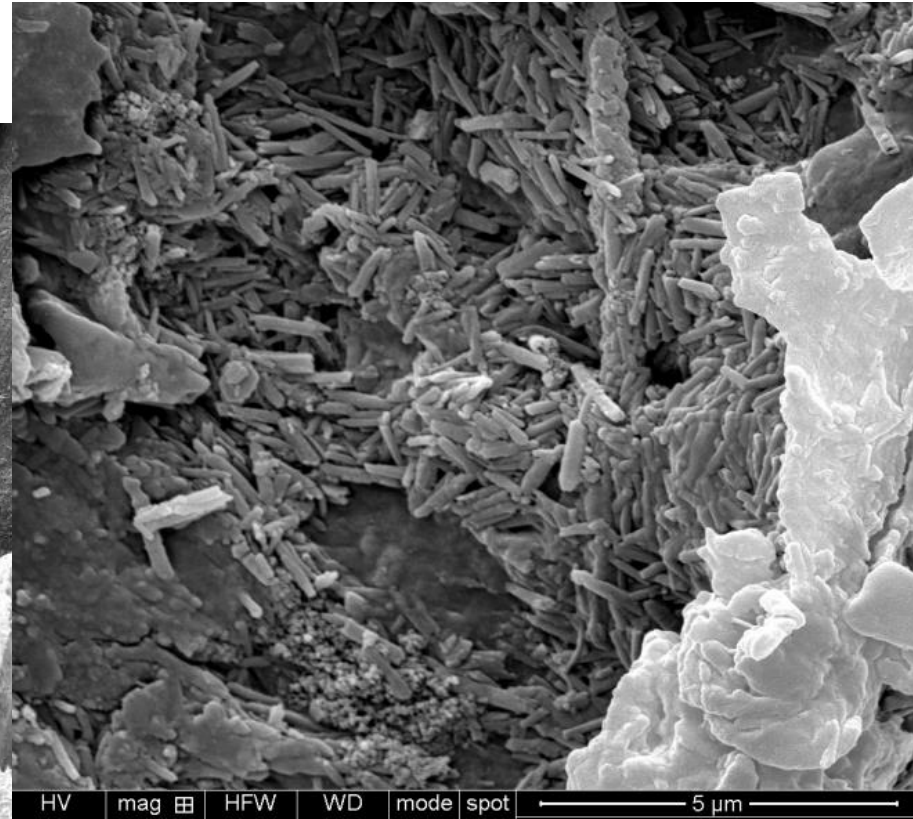
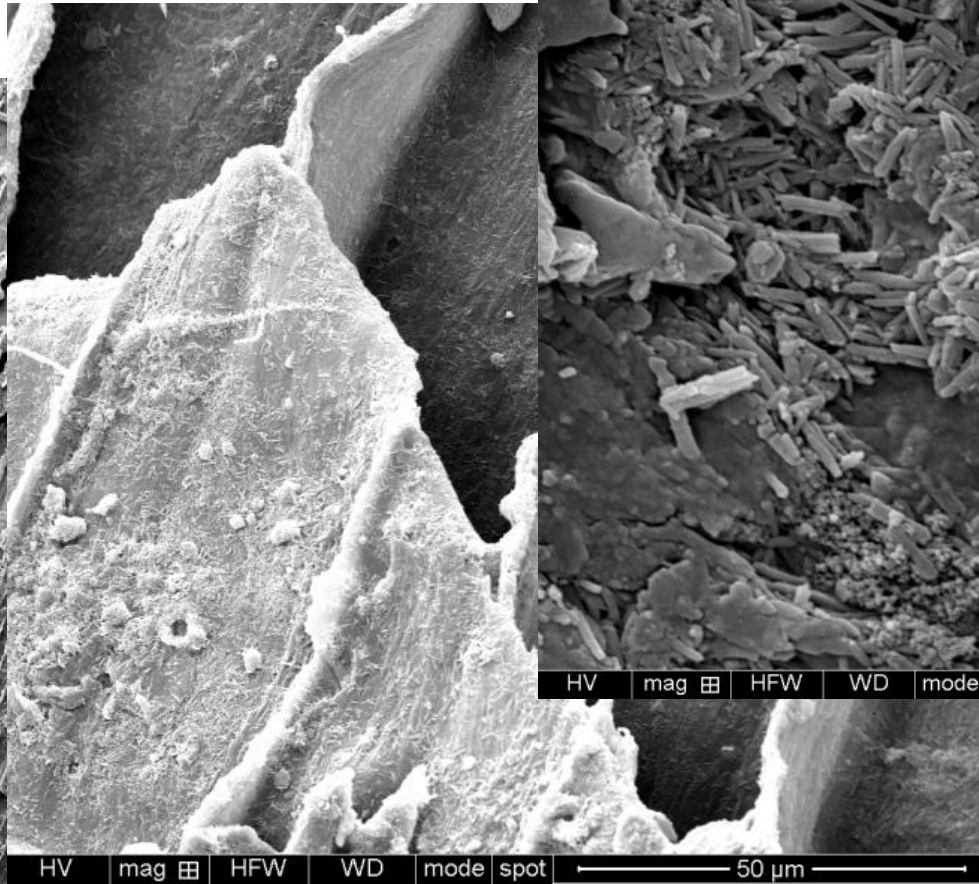
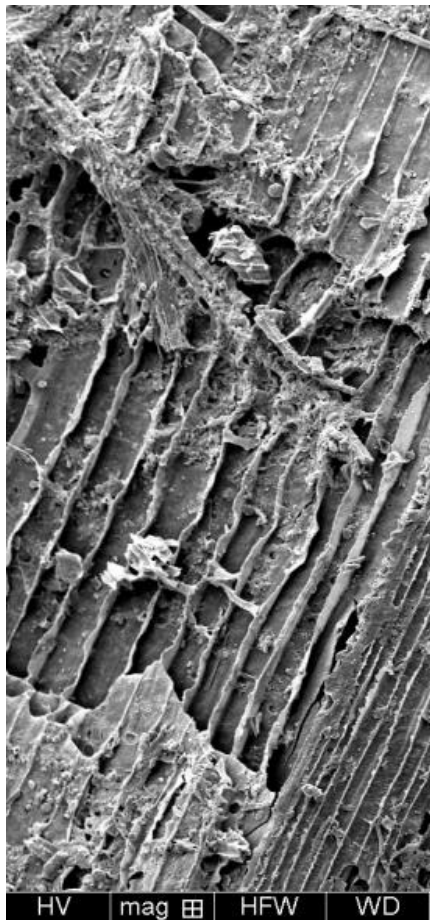
Tan δ data for beeswax/HNT



Shear



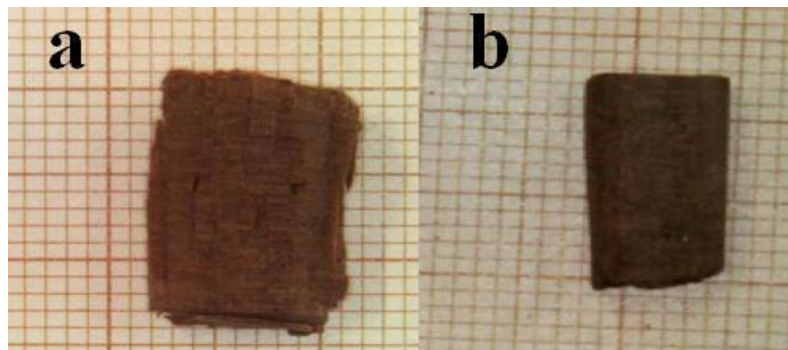
SEM images from waterlogged wood treated with beeswax/HNT



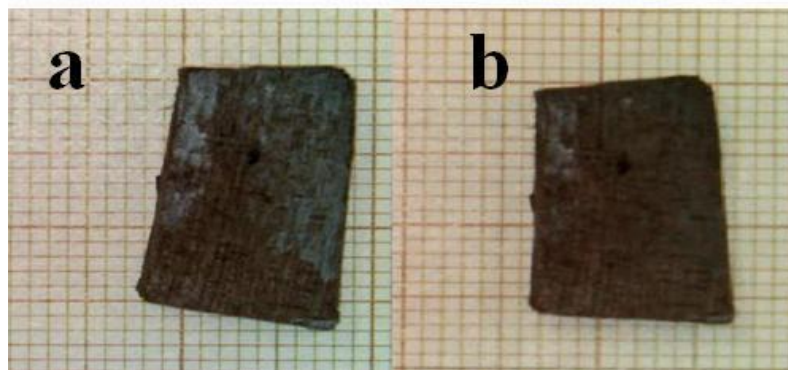
Waterlogged Archaeological Woods shrinking effect

Before drying

After drying



Untreated sample



Sample treated with
beeswax/HNT

HNT% in the dried consolidant	ΔV (%)
Untreated wood	40,6
0	11,61
30	6,2

Metodi

Analisi termica: TGA, DMA, DSC, micro-DSC

Termodinamica in soluzione: nano-ITC, velocità del suono, densità, osmometria

Large facilities: SANS

Superficie: angolo di contatto, tensione superficiale

Collaborations

TU-Berlin { • Prof. M. Gradzielski

ILL-Grenoble { • Dr. I. Grillo

Kazan Federal University { • Prof. R. F. Fakhrullin

La-Tech { • Prof. Y. Lvov

Monash University { • Dr. P. Pasbakhsh